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Critical conditions for the wetting of soils

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Abstract

The wettability of soil is of great importance for plants and soil biota and in determining whether flooding and soil erosion will occur. The analysis used in common measurements of soil hydrophobicity makes the assumption that water always enters soils if the average contact angle between the soil and water is 90° or lower; these tests have been used for decades. The authors show theoretically and experimentally that water cannot enter many soils unless the contact angle is considerably lower than this, down to approximately 50°. This difference generates serious errors in determining and modeling soil wetting behavior.

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Soil water repellency reduces or inhibits wetting of soils. It originates from organic compounds with hydrophobic properties released during organic matter decomposition, wildfires or contamination with hydrocarbons and is observed in many soils following dry periods. It has far-reaching environmental and economic implications including enhanced flooding and soil erosion, poor crop or turf performance, accelerated preferential flow and groundwater contamination, but also reduced evaporation and protection of soil carbon against oxidation[1, 2]. To assess soil water repellency, molarity of ethanol drop (MED), percentage ethanol (%Ethanol), or the related Critical Surface Tension (CST) test are often used[3-5]. In surface science, a Young's Law solid/water contact angle θ_e=90° is the boundary between a hydrophilic and hydrophobic solid. In soil science, it is assumed that the same threshold indicates when the soil matrix will wet[3, 6, 7]. This assumption is applied to calculate physical parameters from measured data[3, 4], despite evidence that lower local contact angles can give rise to high apparent contact angles[8, 9] and some questioning of its validity[10]. Here we demonstrate from surface free energy considerations that this critical assumption is erroneous: a soil surface may be non-wettable for values substantially lower than 90°.

A 90° threshold is based on the assumption that porous media behave similarly to a bundle of capillary tubes, but this is a poor approximation to the shapes of voids created by grains of soil. An alternative model of soil is the 111 plane of close packed (hcp or ccp) identical spheres of radius *R*. Such a model has previously been considered for imbibition of liquids into powders.[11] The capillaries are then formed by the voids between three touching spheres and these do not possess parallel sides. As a liquid penetrates down a void, changes occur in the relative proportions of the solid-liquid and

liquid-vapor interfacial areas. Marmur has previously noted that such local variations in the structure of a porous medium modify the extent of capillary rise by their effect on changes in solid-liquid interfacial area with respect to volume and solid-liquid interfacial area.[12] He used a general formulation, independent of a specific geometrical structural model such as close packed spheres, by using concepts of local porosity and specific area. Constrictions in channels like this are used by plants to protect their stomata from flooding by wetting liquids.[13]

Surface free energy changes during wetting of an array of close packed spheres, of radius *R*, can be estimated using a basic repeating cell of a void surrounded by a triangle linking the centers of the three adjacent spheres, and approximating the liquid meniscus to a horizontal plane (Fig. 1(a)). This approximation is valid for droplets with spherical radius much greater than the size of void between spheres so that the meniscus curvature due to the Laplace excess pressure may be neglected; these boundaries are usually observed when making MED or water drop penetration time (WDPT) measurements. The solid-liquid surface area and liquid-vapor surface areas are then:

$$A_{SL} = \pi R h \qquad \text{and} \qquad A_{LV} = \sqrt{3}R^2 - \frac{\pi\left(2hR - h^2\right)}{2} \tag{1}$$

For a change in penetration depth Δh, the change in surface free energy is therefore:

$$\Delta F = \left(\gamma_{SL} - \gamma_{SV}\right)\Delta A_{SL} + \gamma_{LV}\Delta A_{LV} \tag{2}$$

where the γ_{ij} are the interfacial energies. Using Young's Law, $\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$, gives:

$$\Delta F = -\pi R \gamma_{LV}\left[\cos\theta_e + \left(1 - \frac{h}{R}\right)\right]\Delta h \tag{3}$$

and the equilibrium depth of penetration is therefore $h_e=R(1+\cos\theta_e)$ [Fig. 1(b)], providing the penetrating meniscus does not encounter the top of a sphere from the layer below. This is the same as the result calculated by making the local angle equal to θ_e.[14, 15]

From the geometry of the close packed spheres, the top of the second layer lies at a depth $h_e=2(2/3)^{1/2}R$. The second layer can be considered in the same way as the first, although the spheres are displaced relative to the top layer. Calculating the free energy from the top of the second layer to the bottom of the first in a similar manner as above shows that for all values of θ_e where the meniscus spontaneously touches a sphere from the layer below, the surface free energy will be reduced by the meniscus further advancing into the spherical bead structure. This means that the lowest possible angle that a liquid can sit on a surface of spheres without penetrating fully is just below the angle where it touches the second layer, giving a critical penetration depth $h_c=2(2/3)^{1/2}R$ and critical contact angle of $\theta_e{}^c=50.73°$. If the surface free energy is plotted against h this is the highest contact angle at which no secondary minimum occurs. This result is the same as given by Bán *et al*. who argued that the necessary condition for "upward" imbibition into a close packed bead bed was that the liquid surface needs to rise to at least the height of the second layer of beads before the curvature of the meniscus vanishes.[11] The assumptions used break down if the particles are large enough that the gaps approach the capillary length of the liquid used, in which case imbibition will occur at higher contact angles.

The calculation of the critical contact angle was tested using a range of liquids on model soils consisting of beds of fluorocarbon-coated spherical silica beads or sand;

fluorocarbon was chosen to minimize the contact angle hysteresis. Silica spheres (75 µm diameter) and acid-washed sand were obtained from Aldrich (UK); glass slides (Scientific Glass Labs, China) were used as flat substrates. Sand and spheres were washed in 30% HCl (Fisher) for 8 hours three times and then rinsed five times with deionised water before being dried in a vacuum oven at 80°C for 3 hours. All substrates were coated with fluorocarbon using 'Extreme Wash-in Solution' (Grangers, UK). The solution was diluted 1:20 with deionised water; substrates were added (5 g/20 ml), stirred and allowed to stand for 10 min before being rinsed three times with deionised water. The samples were allowed to air dry before final drying in a vacuum oven at 80° C for 3 h.

Contact angles were measured on coated glass slides, using a Krüss DSA 10 Mk II instrument to place 5 µL droplets of liquid on the substrates inside a closed chamber saturated with the liquid being used. Droplets with such a small volume ensure experiments are consistent with the model assumption of zero hydraulic pressure and an imbibition process driven by surface free energy changes. Test liquids used were *n*-octane, *n*-heptane, *n*-hexane and *n*-pentane (99+%, Aldrich). Drops were photographed 2 s after placement and contact angles analyzed using instrument software fitting the drop outline to a circular arc. Particle and sand bed penetration measurements were carried out in the same closed chamber by placing the smallest possible drops (around 10 µL) carefully onto the beds of particles; these experiments were filmed using the DSA 10.

On the coated spheres the critical contact angle for penetration was found to occur between the contact angles for pentane and hexane, 52°-61° (Fig. 2); these results are consistent with Bán *et al*. who found critical angles in the range 49.5^{o}-57.7^{o} for

imbibition of ethanol into powder beds of sulfur, polyamide and PTFE and for silylated glass beads; they also compared upward and downward imbibition with a 2 cm head and observed no difference suggesting that the meniscus of the test solutions in the particle beds was close to horizontal. The higher measured angle than the theoretical value is likely to be due to the particles not being uniform in size[8] although differences between the measured (pseudo) advancing contact angle and the equilibrium contact angle assumed in the theory might also account for the difference. The particles were large enough that when penetration occurred it was very rapid, whereas drops remaining on the surface were stable. Although spherical particles provide a simple model for soil, real soil particles are not spherical and have relatively wide size distributions, so the experiment was repeated on sand coated with fluorocarbon; the critical angle for entry into sand was between hexane and heptane, 61°-65°. Real soils consist of a mixture of particles of different types, inducing wetting fingers along more hydrophilic areas. If these fingers are large compared to the particles they are likely to behave locally similarly to the homogenous beds of particles described in this letter. The effect is therefore general, although spherical particles with low contact angle hysteresis are a special case where results are expected to be reasonably close to the theoretical critical angle regardless whether advancing or equilibrium contact angles are measured.

The fact that the contact angle of liquids at penetration into a particle bed is considerably less than 90° and varies with particle shape will generate a large error if CST is used to calculate the surface energy of soils. This may result in erroneous outcomes in the classification and modeling of flow and transport through soils. Agreement between values estimated from CST tests and capillary rise measurements[3] or

water retention measurements[14] may arise when the assumption that soil is made up of parallel capillaries is made throughout. If soils of different particle shapes or size distributions are compared, the critical θ_e^c may vary. The common assumption that a liquid will enter a soil for contact angles of just less than 90° was found to be false for beds of chemically identical spherical particles or sand, invalidating calculations using this assumption for soils.

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Figure Legends

Figure 1. (a) Repeating cell in 111 plane of a close-packed surface of spheres consisting of a triangle of side length *2R* with 3×1/6 segments of particles. This allows calculation of liquid-air interfacial area at different penetration depths if the meniscus is approximated as a horizontal plane (b) liquid with contact angle θ less than 90° suspended at equilibrium on a bed of spheres.

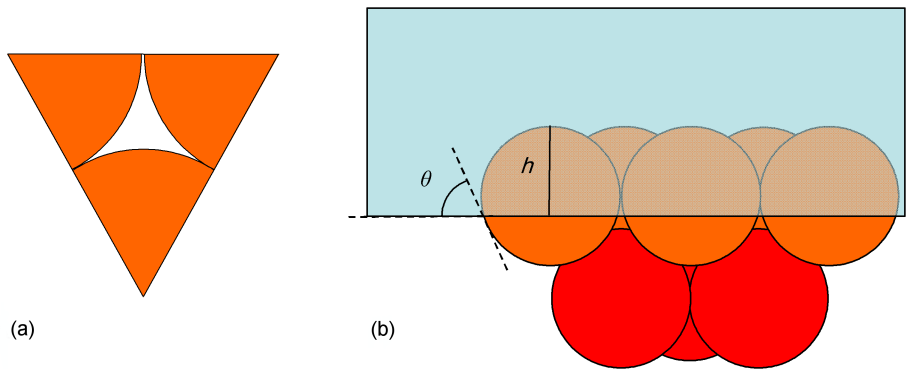

Figure 2. 10 µl droplet of hexane on a bed of fluorocarbon coated 75 µm diameter glass spheres (left) and 5 µl droplet of hexane on a flat surface of the same type showing a contact angle of around 61° (right).